

**THERMAL EXTENSIONS AND POLYMORPHOUS TRANSITIONS IN  
Cu<sub>2-x</sub>A<sub>x</sub>Se (x=0, 0.2, 0.4; A=Ag, Zn), CuAgSe, CuAgSe<sub>0.5</sub>(S,Te)<sub>0.5</sub> CRYSTALS**

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The single crystals Cu<sub>2-x</sub>A<sub>x</sub>Se (x=0, 0.2, 0.4; A=Ag, Zn), CuAgSe, CuAgSe<sub>0.5</sub>(S,Te)<sub>0.5</sub> have grown up by Bridgeman method and synthesized; all existing polymorphous transformations have fixed by the method of high-temperature roentgen diffractometry in temperature interval 290-1000K. From temperature dependence of lattice parameters the thermal expansions are calculated by the main crystallographic directions.

Among many applications of the method of high-temperature roentgenography in physics of materials, the study of polymorphous transformations and thermal expansions is important one. It is impossible to discuss the material polymorphism without results of high-temperature roentgenographic investigations. The material thermal expansion is usually studied by dilatometry method. However, the possibility of carrying out the investigation on the sample is the advantage of the method of high-temperature roentgenography. The anisotropy study of thermal expansion not only on micro-crystalline but on semi-crystalline samples and also in phase mixture can be carried out with the help of method of high-temperature roentgenography. The "roentgen diffractometry" gives the possibility to differentiate the phase transitions of I and II type that is very difficult by the methods of usual dilatometry as even so precision dilatometers under their persistence can't differ the measurement of sample length with temperature  $l=f(T)$  at phase transitions from discontinuous change of curve  $l=f(T)$  at phase transitions of I type. Below the results of polymorphous transformation study and the calculations of thermal expansions by the main crystallographic directions of modifications existing in the crystals of above mentioned compositions are given.

The synthesis Cu<sub>2-x</sub>A<sub>x</sub>Se (x=0, 0.2, 0.4; A=Ag, Zn), CuAgSe, CuAgSe<sub>0.5</sub>(S,Te)<sub>0.5</sub>, physicochemical analysis and growing up of single crystals are described in works [1,2] in detail.

The single crystals of above mentioned compositions are investigated on ДРОН-3М diffractometer (CuK<sub>α</sub> is radiation,  $\lambda_{\alpha}=1,5418 \text{ \AA}$ , Ni is filter) with high-temperature attachment YPBT-2000 providing the vacuum  $10^{-2} \text{ Pa}$ , angular resolution

of record is  $\sim 0,1^{\circ}$ , the mistake of reflection angle definition doesn't exceed  $\Delta\theta=\pm 0,02^{\circ}$ .

**1. Cu<sub>2</sub>Se.** Cu<sub>2</sub>Se single crystals are easily chipped in direction [001]. The six clear diffraction peaks with (001), (022), (027), (040), (055) and (0.0.18) are fixed from crystals at room temperature in angle interval  $10^{\circ} \leq 2\theta \leq 90^{\circ}$ . Not changing this crystal orientation the stove is switched on and the records are made in temperature interval 290-573K. All diffraction reflections higher 423K belong to low-temperature orthorhombic modification disappear and the diffraction reflections with indexes (111), (222) and (333) belonging to high-temperature HCC modification are fixed in previous temperature interval. It is established that balance temperature between modifications  $T_0=407 \pm 1 \text{ K}$ .

The calculation of lattice parameters of orthorhombic and HCC modifications is given in table 1 and graphically on the fig.1.

From values of lattice parameters the thermal expansion along main crystallographic directions which is given in table 2, has been calculated.

The dependences of strengths of orthorhombic and HCC modifications on temperature shows that strength at equilibrium temperature of  $T_0=407 \text{ K}$  modifications changes by jump  $0,061 \text{ g/sm}^3$ .

Note that the concentration change takes place in the dependence on transformation multiplicity, i.e. Cu<sub>2</sub>Se → Cu<sub>2-x</sub>Se (x=0,20) transition takes place with cuprum extraction on Cu<sub>2-x</sub>Se block boundaries. This non-stoichiometric composition also has HCC lattice with parameter  $a=5.740 \text{ \AA}$ . This composition is stable in temperature region from room one up to melting point.

Crystallographic parameters of Cu<sub>2</sub>Se at different temperatures.

Table 1.

$T_{exp}, \text{ K}$	Modification	Lattice parameters, $\text{ \AA}$			$Z$	Sp. gr.	$V, \text{ \AA}^3$	$\rho, \text{ gr/cm}^3$
		$a$	$b$	$c$				
293	Orthorhombic	4.117	7.032	20.347	12	P222 <sub>1</sub>	589.061	6.968
323	Orthorhombic	4.118	7.034	20.351	12	P222 <sub>1</sub>	589.487	6.963
373	Orthorhombic	4.121	7.038	20.367	12	P222 <sub>1</sub>	590.716	6.948
405	Orthorhombic	4.125	7.042	20.380	12	P222 <sub>1</sub>	592.003	6.933
423	HCC	5.839			4	$F\bar{4}3m$	199.074	6.827
473	HCC	5.844			4	$F\bar{4}3m$	199.586	6.855
523	HCC	5.855			4	$F\bar{4}3m$	200.715	6.816
573	HCC	5.862			4	$F\bar{4}3m$	201.436	6.792

Table 2.

Thermal expansion of orthorhombic and HCC modifications of Cu<sub>2</sub>Se crystal.

T, K	$\alpha_{[100]} \cdot 10^6 K^{-1}$	$\alpha_{[010]} \cdot 10^6 K^{-1}$	$\alpha_{[001]} \cdot 10^6 K^{-1}$	$\bar{\alpha} = \frac{\alpha_{[100]} + \alpha_{[010]} + \alpha_{[001]}}{3} \cdot 10^6 K^{-1}$	$\beta = \alpha_{[100]} + \alpha_{[010]} + \alpha_{[001]} \cdot 10^6 K^{-1}$
293-323	8.097	9.480	6.553	8.043	24.130
293-373	12.145	10.666	12.287	11.699	35.098
293-405	17.350	12.697	14.481	14.843	44.528
423-473	17.126			17.126	51.378
423-523	27,402			27,402	82.206
423-573	26,260			26,260	78.780

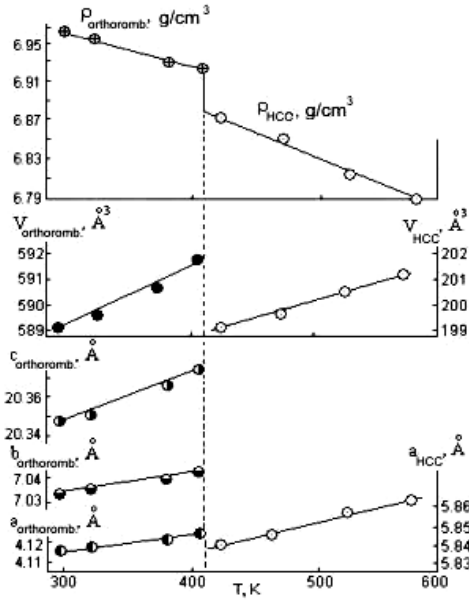


Fig. 1. Temperature dependence of lattice parameters, volume and strength of orthorhombic and HCC modifications of Cu<sub>2</sub>Se.

**2. Cu<sub>1.80</sub>Zn<sub>0.20</sub>Se.** Cu<sub>1.80</sub>Zn<sub>0.20</sub>Se single crystals are easily chipped on [011] directions. The six diffraction reflections which are indicated on the base of parameters of orthorhombic and HCC modifications are fixed at room temperature in 30° ≤ 2θ ≤ 70° angle interval from such samples, i.e. the high-temperature HCC modification is stabilized at room temperature.

The parameters of elementary cell of orthorhombic modifications are calculated from reflections with (009), (0 0 10), (1 0 10), (042), (043) and (044) and HCC modifications from (220), (311) and (222) reflections in temperature region 290-870K which are given in table 3 and graphically shown on fig.2. The thermal expansions are calculated from lattice parameters of both modifications (table 4).

As it is seen from fig.2 the lattice parameters of orthorhombic and HCC modifications in the dependence on temperature linearly increase. The strengths of both modifications in the dependence on temperature linearly decrease and the strength of HCC modification is more than the strength of orthorhombic one, i.e. Δρ = ρ<sub>cr</sub> - ρ<sub>orthor</sub> = 0.25 gr/cm<sup>3</sup>.

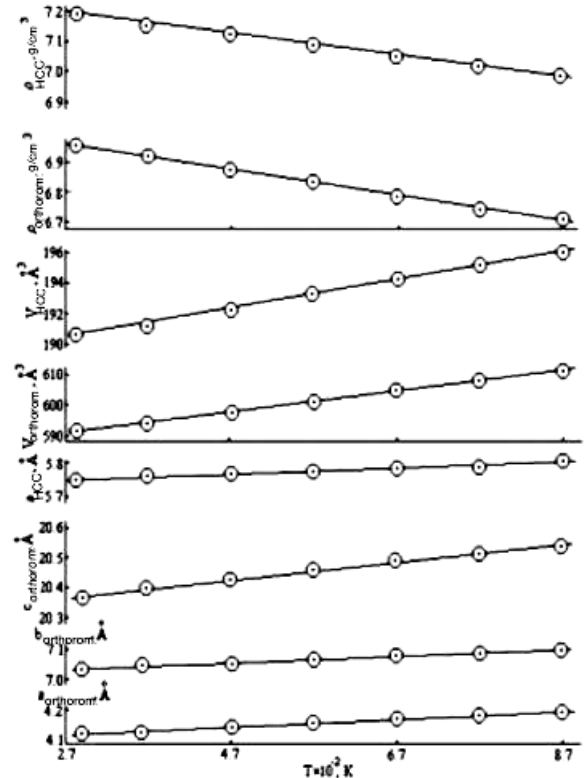


Fig. 2. Temperature dependence of lattice parameters of orthorhombic and HCC modifications of Cu<sub>1.80</sub>Zn<sub>0.20</sub>Se.

Table 3.

Crystallographic parameters of Cu<sub>1.80</sub>Zn<sub>0.20</sub>Se at different temperatures.

T <sub>exp</sub> , K	Modification	Lattice parameters, Å			Z	Sp. gr.	V, Å <sup>3</sup>	ρ, g/cm <sup>3</sup>
		a	b	c				
290	Orthorhombic	4.127	7.033	20,362	12	P222 <sub>1</sub>	591.011	6.957
	HCC	5.756			4	Fm3m	190.705	7.187
370	Orthorhombic	4.131	7.049	20,409	12	P222 <sub>1</sub>	594.298	6.919
	HCC	5.765			4	Fm3m	191.601	7.153
470	Orthorhombic	4.149	7.054	20,439	12	P222 <sub>1</sub>	598.189	6.875
	HCC	5.772			4	Fm3m	192.300	7.126
570	Orthorhombic	4.156	7.070	20,471	12	P222 <sub>1</sub>	601.498	6.836
	HCC	5.782			4	Fm3m	193.301	7.091
670	Orthorhombic	4.167	7.088	20,506	12	P222 <sub>1</sub>	605.659	6.790
	HCC	5.793			4	Fm3m	194.406	7.050
770	Orthorhombic	4.189	7.089	20,517	12	P222 <sub>1</sub>	609.269	6.749
	HCC	5.802			4	Fm3m	195.314	7.018
870	Orthorhombic	4.196	7.102	20,535	12	P222 <sub>1</sub>	611.943	6.720
	HCC	5.819			4	Fm3m	196.224	6.985

Table 4.

Thermal expansion of orthorhombic and HCC modifications of Cu<sub>1.80</sub>Zn<sub>0.20</sub>Se crystal.

T, K	$\alpha_{[100]} \cdot 10^6 K^{-1}$	$\alpha_{[010]} \cdot 10^6 K^{-1}$	$\alpha_{[001]} \cdot 10^6 K^{-1}$	$\bar{\alpha} = \frac{\alpha_{[100]} + \alpha_{[010]} + \alpha_{[001]}}{3} \cdot 10^6 K^{-1}$	$\beta = \alpha_{[100]} + \alpha_{[010]} + \alpha_{[001]} \cdot 10^6 K^{-1}$
290-370	12.115	28.437	28.853	23.135	69.405
290-470	29.615	16.588	21.009	22.404	67.212
290-570	25.096	18.789	19.118	21.001	63.003
290-670	25.506	20.580	18.611	21.566	64.697
290-770	31.298	16.588	15.859	21.248	63.745
290-870	28.826	16.915	14.659	20.130	60.390
290-370	19.545			19.545	58.635
290-470	15.443			15.443	46.329
290-570	16.332			16.332	48.996
290-670	16.916			16.916	50.748
290-770	16.649			16.649	49.947
290-870	16.425			16.475	49.425

**3. CuAgSe.** CuAgSe compound forms at Cu<sub>2</sub>Se-Ag<sub>2</sub>Se=1:1 relation on peritectic reaction at temperature 1033K [3]. The structure of low-temperature phase CuAgSe in [3] is determined as tetragonal one with lattice parameters  $a=4.083\text{Å}$ ,  $c=6.30\text{Å}$ ,  $Z=2(\text{CuAgSe})$ , P4/nmm and  $\rho=7.91\text{gr/cm}^3$ . In [4] the crystalline structure CuAgSe is determined as orthorhombic one with lattice parameters  $a=4.105\text{Å}$ ,  $b=20.35\text{Å}$ ,  $c=6.31\text{Å}$ ,  $Z=10$  and  $\rho=7.885\text{gr/cm}^3$ . The last one is superstructural tetragonal lattice. The orthorhombic lattice parameter  $b$  is multiple to five tetragonal lattice parameters  $b$  ( $b_p=5b_m$ ). According to data [4] Ag atoms in orthorhombic structure CuAgSe are in planes perpendicular to axis  $c$ . 4 Ag are on distance 2,96 Å and 6Se are on distances 2.67 Å (4Se), 3,59 Å (1Se) and 3,64 Å (1Se). Se atoms form the extended tetrahedrons in centers of which Cu atoms are. The distance is Se-Se=3.03 Å, Cu-Se=2.06-2.50 Å and the least distance is Cu-Ag=2.98 Å.

In [5] it is shown that orthorhombic modification at 504K transforms into high-temperature HCC modification with elementary cell parameter  $a=6.082\text{Å}$ .

The 11 clear diffraction reflections are fixed at room temperature from CuAgSe single crystals in  $10^\circ \leq 2\theta \leq 90^\circ$  angle interval. All fixed reflections are clearly indicated on the base of orthorhombic lattice parameters. The 11 diffraction reflections fixed at room temperature up to

temperature 495K stay constant. At 545K all 11 diffraction reflections disappear and four new reflections from planes with indexes (111), (200), (220) and (311) of high-temperature HCC modification with elementary cell parameters:  $a=6.082\text{Å}$ ,  $Z=4$ , sp. gr. Fm3m and  $\rho=7.389\text{gr/cm}^3$  are fixed in the previous angle interval. The equilibrium temperature between modifications is equal to  $T_0=504\pm 1\text{K}$ .

The transformations in CuAgSe are reversible ones and take place by type of single crystal – single crystal.

The temperature dependence of lattice parameters is presented in table 5 and graphically on fig.3. As it is seen from fig.3 all three parameters of orthorhombic and  $a$  parameter of HCC modifications in the dependence on temperature linearly increase.

The thermal expansion coefficients (table 6) have been calculated from temperature dependence of lattice parameters of orthorhombic and HCC modifications in 295-595K temperature interval.

As it is seen from table 6 the linear expansion coefficient of orthorhombic modification on crystallographic direction [010] strongly differs from [100] and [001] ones. From this it is followed that the existence of anisotropic thermal expansion is the one of reasons of temperature instability of low-temperature modification CuAgSe.

Table 5.

Crystallographic parameters of CuAgSe at different temperatures.

$T_{exp}, K$	Modification	Lattice parameters, Å			Z	Sp. gr.	$V, \text{Å}^3$	$\rho, \text{gr/cm}^3$
		$a$	$b$	$c$				
295	Orthorhombic	4.104	20.350	6.310	10	P4/nmm	526.988	7.888
345	Orthorhombic	4.111	20.412	6.321	10	P4/nmm	530.419	7.837
395	Orthorhombic	4.116	20.515	6.337	10	P4/nmm	535.095	7.768
445	Orthorhombic	4.125	20.565	6.349	10	P4/nmm	538.590	7.718
495	Orthorhombic	4.130	20.614	6.366	10	P4/nmm	541.975	7.669
504	HCC	6.069			4	Fm3m	223.538	7.436
545	HCC	6.082			4	Fm3m	224.978	7.389
595	HCC	6.097			4	Fm3m	226.646	7.334

Table 6.

Thermal expansion of orthorhombic and HCC modifications of CuAgSe crystal.

T, K	$\alpha_{[100]} \cdot 10^6 K^{-1}$	$\alpha_{[010]} \cdot 10^6 K^{-1}$	$\alpha_{[001]} \cdot 10^6 K^{-1}$	$\bar{\alpha} = \frac{\alpha_{[100]} + \alpha_{[010]} + \alpha_{[001]}}{3} \cdot 10^6 K^{-1}$	$\beta = \alpha_{[100]} + \alpha_{[010]} + \alpha_{[001]} \cdot 10^6 K^{-1}$
295-345	34.113	60.934	34.865	43.304	129.912
295-395	29.240	81.081	42.789	51.037	153.110
295-445	34.113	70.434	41.204	48.584	145.751
295-495	31.676	64.865	44.374	46.972	140.915
504-545	52.245			52.245	156.735
504-595	50.699			50.699	152.097

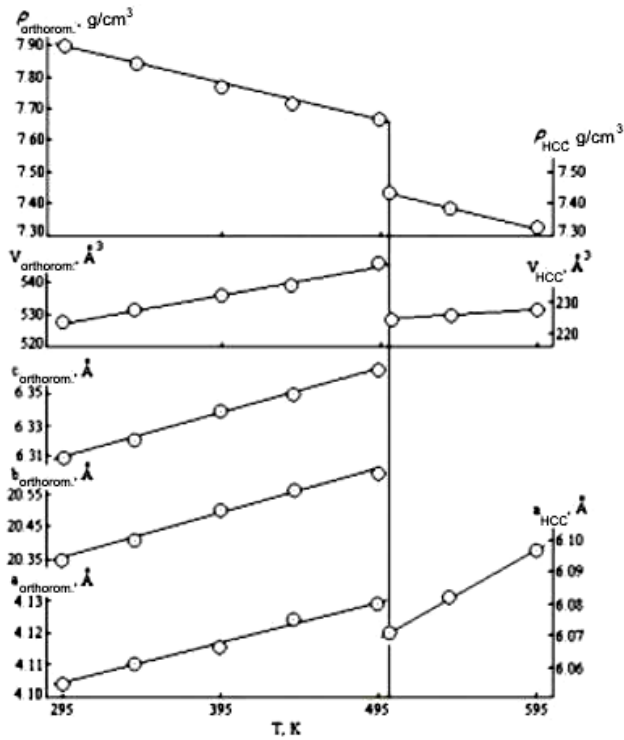


Fig.3. Temperature dependence of lattice parameters, volume and strength of orthorhombic and HCC modifications of CuAgSe.

The fact that polymorphous transformations in Cu<sub>2</sub>Se and Ag<sub>2</sub>Se compounds have reflected on triple compound is the another reason of temperature instability of low-temperature modification. Note that the value of lattice

parameters of low-temperature orthorhombic modification CuAgSe approximately corresponds to the values of lattice parameters of low-temperature orthorhombic modification Cu<sub>2</sub>Se:  $a=4.118 \text{ \AA}$ ,  $b=7.032 \text{ \AA}$ ,  $c=20.381 \text{ \AA}$ .

In crystalline structure Cu<sub>2</sub>Se Cu atoms are statistically distributed in tetrahedral spaces formed by Se atoms; in CuAgSe structure Ag atoms are distributed in the planes perpendicular to  $c$  axis and Cu atoms as in Cu<sub>2</sub>Se are in the center of tetrahedrons formed by Se atoms. These structural differences and formed additional bonds Cu-Ag and Ag-Se are also the reason of increase of transformation temperature in CuAgSe ( $T_0=504\text{K}$ ) in comparison with Cu<sub>2</sub>Se ( $T_0=407\text{K}$ ) and Ag<sub>2</sub>Se ( $T_0=408\text{K}$ ).

**4. Cu<sub>1.6</sub>Ag<sub>0.4</sub>Se.** The 18 clear diffraction reflections the 14 of which are indicated on the base of parameters of orthorhombic modification CuAgSe and the rest four and seven from fourteen are also indicated on the base of parameters of orthorhombic modification Ag<sub>2</sub>Se, have fixed at room temperature from crystalline ingot Cu<sub>1.6</sub>Ag<sub>0.4</sub>Se of optional orientation in  $10^\circ \leq 2\theta \leq 110^\circ$  angle interval.

From this it follows that Cu<sub>1.6</sub>Ag<sub>0.4</sub>Se crystals at room temperature are two-phase ones.

The stove had been switched on and through each 50K the control diffraction records had been carried out after record of diffraction reflections at room temperature. The changes in temperature interval 293-523K in numbers and diffraction reflection intensities don't take place. At 573K all diffraction reflections disappear and 7 new reflections belonging to high-temperature HCC modification with elementary cell parameter  $a=5896 \text{ \AA}$  are fixed in previous angle interval.

Table 7.

Crystallographic parameters of Cu<sub>1.6</sub>Ag<sub>0.4</sub>Se at different temperatures.

$T_{exp}$ , K	Modification	Lattice parameters, $\text{\AA}$			Z	Sp. gr.	$V$ , $\text{\AA}^3$	$\rho$ , $\text{gr/cm}^3$
		$a$	$b$	$c$				
293	CuAgSe-orthoromb.	4.104	20.350	6.310	10	P4/nmm	526.988	7.885
	Ag <sub>2</sub> Se-orthoromb.	4.333	7.062	7.764	4	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	237.576	8.237
373	CuAgSe-orthoromb.	4.105	20.396	6.318	10	P4/nmm	528.978	7.858
	Ag <sub>2</sub> Se-orthoromb.	4.340	7.089	7.765	4	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	238.900	8.192
473	CuAgSe-orthoromb.	4.120	20.453	6.301	10	P4/nmm	530.962	7.828
	Ag <sub>2</sub> Se-orthoromb.	4.361	7.126	7.773	4	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	241.558	8.101
523	CuAgSe-orthoromb.	4.153	20.533	6.312	10	P4/nmm	538.247	7.723
	Ag <sub>2</sub> Se-orthoromb.	4.424	7.172	7.759	4	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	246.185	7.949
573	Cu <sub>1.6</sub> Ag <sub>0.4</sub> Se-HCC	5.896			4	Fm3m	204.962	7.250
673	Cu <sub>1.6</sub> Ag <sub>0.4</sub> Se-HCC	5.903			4	Fm3m	205.692	7.223

The transformation temperature which is equal to  $T_{tr}=540 \pm 2\text{K}$  has been established. The reversible transformation takes place by the type single crystal–single crystal. The temperature dependences of lattice parameters of both orthorhombic and HCC modifications in temperature interval 293-673K are given in table 7 and they are presented graphically on fig.4.

As it is seen from fig.4 the modification parameters at 473K crystallizing in Ag<sub>2</sub>Se structure strongly deviate from linearity and  $a$  and  $b$  modification parameters crystallizing in Ag<sub>2</sub>Se structure;  $c$  parameter saves the linearity up to transformation temperature. The parameter deviation from linearity at 473K of both orthorhombic phases is mainly connected with redistribution of two types of cations.

The temperature dependences of strength of existing phases are presented on fig.4. The difference of strengths of both modifications at transformation of low-temperature orthorhombic modification CuAgSe and Ag<sub>2</sub>Se into unique HCC modification is:  $\Delta\rho=0.70 \text{ gr/cm}^3$  and  $\Delta\rho_2=0.47 \text{ gr/cm}^3$  correspondingly. As it has been mentioned this leads to single crystal – single crystal transformation.

The thermal expansion coefficients calculated from temperature dependence of lattice parameters of existing modifications in Cu<sub>1.6</sub>Ag<sub>0.4</sub>Se composition are given in table 8. As it is seen from table 8 the thermal expansion coefficients in both orthorhombic phases on main crystallographic directions strongly differ  $\alpha_{[100]} < \alpha_{[010]} < \alpha_{[001]}$ , i.e. the strong anisotropy exists. This is one of the main reasons of temperature instability of crystalline structure.

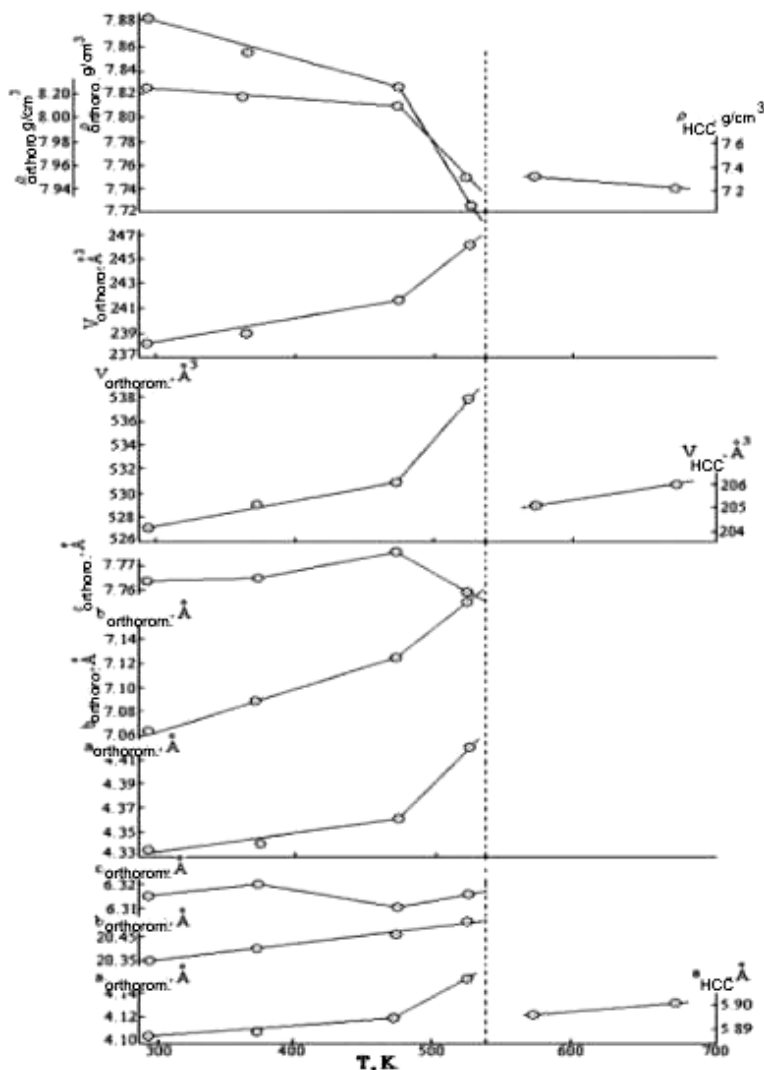


Fig.4. Temperature dependence of lattice parameters, volume and strength of orthorhombic and HCC modifications of  $\text{Cu}_{1.6}\text{Ag}_{0.4}\text{Se}$ .

Table 8.

Thermal expansion of orthorhombic and HCC modifications of  $\text{Cu}_{1.6}\text{Ag}_{0.4}\text{Se}$  crystal.

T, K	$\alpha_{[100]} \cdot 10^6 \text{ K}^{-1}$	$\alpha_{[010]} \cdot 10^6 \text{ K}^{-1}$	$\alpha_{[001]} \cdot 10^6 \text{ K}^{-1}$	$\bar{\alpha} = \frac{\alpha_{[100]} + \alpha_{[010]} + \alpha_{[001]}}{3} \cdot 10^6 \text{ K}^{-1}$	$\beta = \alpha_{[100]} + \alpha_{[010]} + \alpha_{[001]} \cdot 10^6 \text{ K}^{-1}$
293-373	3.046	28.256	15.848	15.717	47.15
293-473	21.659	28.119	7.924	19.234	57.702
293-523	51.911	39.098	1.378	30.796	92.387
293-373	20.194	47.791	1.610	23.198	69.595
293-473	35.900	50.348	6.440	30.896	92.686
293-523	91.311	67.723	-2.800	52.078	156.234
573-673	11.872			11.872	35.616

**5.  $\text{CuAgSe}_{0.5}\text{S}_{0.5}$ .** The 16 clear diffraction reflections, induction of which proves the existence in the sample of two phases the one of which is identical one to low-temperature monoclinic  $\text{Cu}_{1.96}\text{S}$  [6] and other one has the elementary cell of low-temperature orthorhombic  $\text{CuAgSe}$  [4], have fixed at 293K from optionally oriented crystal  $\text{CuAgSe}_{0.5}\text{S}_{0.5}$  in angle interval  $10^\circ \leq 2\theta \leq 100^\circ$ .

The stove had been switched on and through each 100K the control records had been carried out after diffractogram record at room temperature. Note that the reflection number and their intensities fixed at room temperature stay constant with temperature increase. Only at 773K the 9 reflections belonging to high-temperature HCC modification with

elementary cell parameter:  $a=6.356 \text{ \AA}$ ,  $Z=4$ , sp.gr.  $\text{Fm}\bar{3}\text{m}$  in previous angle interval. It has been established that equilibrium balance between modifications is  $T_0=695 \pm 2 \text{ K}$ .

The elementary cell parameters of existing modifications in  $\text{CuAgSe}_{0.5}\text{S}_{0.5}$  crystal in temperature interval 293-973K which are given in table 9 and graphically presented on fig.5 have been calculated from diffractogram.

As it is seen from fig.5 the elementary cell parameters  $a_2$ ,  $b_2$  and  $c_2$  of monoclinic  $\text{Cu}_{1.96}\text{S}$  deviate from linearity at 373K, i.e.  $b_2$  and  $c_2$  parameters strongly increase and  $a_2$  parameter decreases and linearly increases after 373K. The lattice parameters  $a_1$ , and  $c_1$  of modification having the orthorhombic structure  $\text{CuAgSe}$  at 473K deviate from

linearity. In spite of such behavior of lattice parameters of both modifications the essential changes don't take place in diffraction numbers and their intensities in the dependence of temperature.

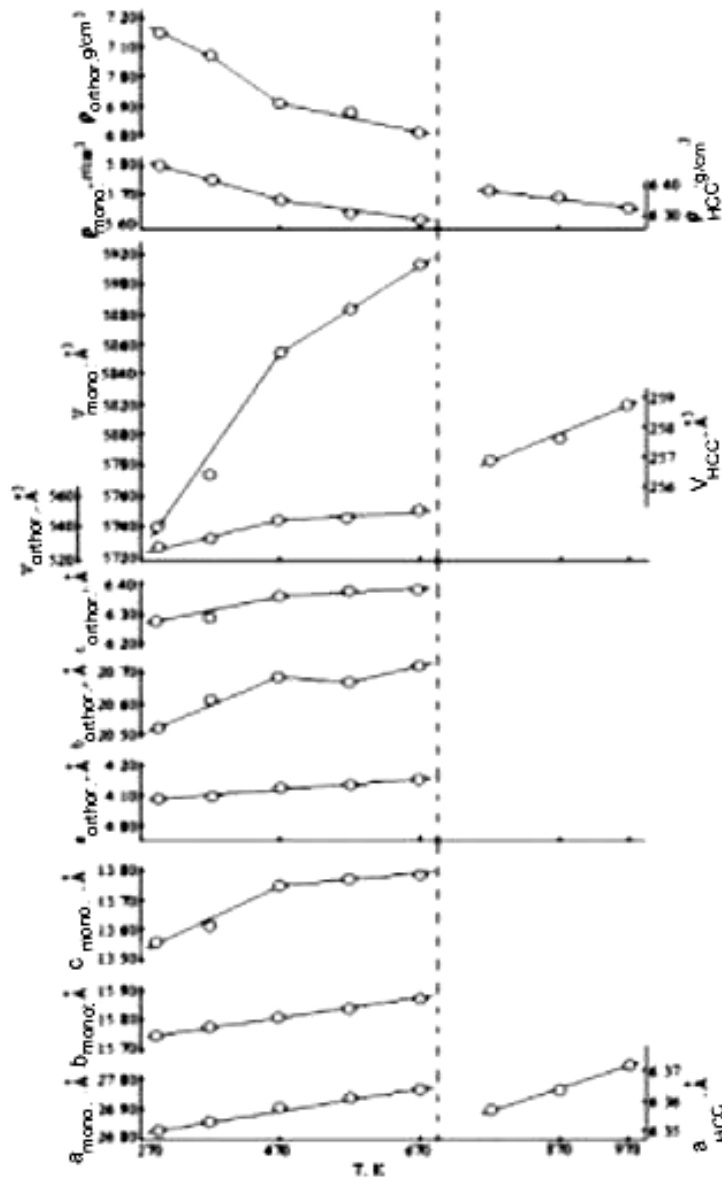


Fig.5. Temperature dependence of lattice parameters, volume and strength of orthorhombic and HCC modifications of  $\text{CuAgSe}_{0.5}\text{S}_{0.5}$ .

Table 9.

Temperature dependence of lattice parameters of modification of  $\text{CuAgSe}_{0.5}\text{S}_{0.5}$  crystal in 293-973K temperature interval.

$T_{exp}$ , K	Modification	Lattice parameters, Å			$\beta$	Z	Sp. gr.	$V$ , Å <sup>3</sup>	$\rho$ , gr/cm <sup>3</sup>
		a	b	c					
293	$\text{Cu}_{1.96}\text{Se}$ -orthorhomb.	26.827	15.745	13.565	90.13°	$8\text{Cu}_{31}\text{S}_{16}$ 10	$P2_1/n$ $P4/nmm$	5729.735 526.564	5.807 7.154
	$\text{CuAgSe}$ -orthorhomb.	4.086	20.524	6.279					
373	$\text{Cu}_{1.96}\text{Se}$ -orthorhomb.	26.867	15.794	13.611	90.13°	$8\text{Cu}_{31}\text{S}_{16}$ 10	$P2_1/n$ $P4/nmm$	5775.656 531.860	5.761 7.083
	$\text{CuAgSe}$ -orthorhomb.	4.103	20.615	6.288					
473	$\text{Cu}_{1.96}\text{Se}$ -orthorhomb.	26.913	15.811	13.763	90.13°	$8\text{Cu}_{31}\text{S}_{16}$ 10	$P2_1/n$ $P4/nmm$	5856.452 545.467	5.682 6.906
	$\text{CuAgSe}$ -orthorhomb.	4.135	20.699	6.373					
573	$\text{Cu}_{1.96}\text{Se}$ -orthorhomb.	26.948	15.847	13.782	90.13°	$8\text{Cu}_{31}\text{S}_{16}$ 10	$P2_1/n$ $P4/nmm$	5885.534 546.672	5.654 6.891
	$\text{CuAgSe}$ -orthorhomb.	4.138	20.681	6.388					
673	$\text{Cu}_{1.96}\text{Se}$ -orthorhomb.	26.971	15.884	13.804	90.13°	$8\text{Cu}_{31}\text{S}_{16}$ 10	$P2_1/n$ $P4/nmm$	5913.735 552.055	5.627 6.824
	$\text{CuAgSe}$ -orthorhomb.	4.163	20.743	6.393					
773	HCC	6.356				4	$Fm\bar{3}m$	256.774	6.376
873	HCC	6.363				4	$Fm\bar{3}m$	257.624	6.355
973	HCC	6.372				4	$Fm\bar{3}m$	258.718	6.328

Table 10.

Thermal expansion of  $\text{CuAgSe}_{0.5}\text{S}_{0.5}$  crystal.

$T, \text{K}$	$\alpha_{[100]} \cdot 10^6 \text{K}^{-1}$	$\alpha_{[010]} \cdot 10^6 \text{K}^{-1}$	$\alpha_{[001]} \cdot 10^6 \text{K}^{-1}$	$\bar{\alpha} = \frac{\alpha_{[100]} + \alpha_{[010]} + \alpha_{[001]}}{3} \cdot 10^6 \text{K}^{-1}$	$\beta = \alpha_{[100]} + \alpha_{[010]} + \alpha_{[001]} \cdot 10^6 \text{K}^{-1}$
293-373	52.007	55.423	17.917	41.782	125.347
293-473	66.623	47.370	83.170	65.721	197.163
293-573	45.451	27.320	61.998	44.923	134.769
293-673	49.592	28.080	47.778	41.817	125.450
293-373	18.638	38.901	42.388	33.309	99.927
293-473	17.810	23.288	81.091	40.730	122.189
293-573	16.109	23.137	57.132	32.126	96.378
293-673	14.126	23.232	46.365	27.908	83.723
773-873	11.013			11.013	33.039
773-973	12.587			12.587	37.761

The thermal expansion coefficients in  $\text{CuAgSe}_{0.5}\text{S}_{0.5}$  composition calculated from temperature dependence of lattice parameters of existing modifications are given in table 10. As it is seen from the table in modification having  $\text{Cu}_{1.96}\text{S}$  structure the thermal structure in [010] direction essentially differs from [100] and [001], i.e.  $\alpha_{[100]} < \alpha_{[010]} > \alpha_{[001]}$ .

Thermal expansion coefficients on the main crystallographic directions of modifications crystallized in  $\text{CuAgSe}$  structure have the anisotropy, i.e.  $\alpha_{[100]} \approx \alpha_{[010]} > \alpha_{[001]}$ .

$\text{CuAgSe}_{0.5}\text{S}_{0.5}$  crystals consisting in two phases deform each other at temperature increase as it is seen from anisotropy of thermal expansion. The germ of HCC modification which grows because of phases forms on the

interface of these phases. The two phases, i.e. crystal transforms into initial state from unique HCC modification at cooling.

**6.  $\text{CuAgSe}_{0.5}\text{Te}_{0.5}$ .** The 22 diffraction reflections which coincide with reflections fixed at from synthesized sample, are fixed at room temperature from optionally oriented crystal  $\text{CuAgSe}_{0.5}\text{Te}_{0.5}$  in angle interval  $10^\circ \leq 2\theta \leq 90^\circ$ . As it is seen from table 11 the crystals of  $\text{CuAgSe}_{0.5}\text{Te}_{0.5}$  composition consist in three phases: I phase is identical one to low-temperature  $\text{Cu}_2\text{Te}$  on elementary cell dimensions; II phase has the elementary cell satisfying to low-temperature phase  $\text{CuAgSe}$  and III cubic phase with diamond-like structure.

Table 11.

Temperature dependence of lattice parameters of modifications of  $\text{CuAgSe}_{0.5}\text{Te}_{0.5}$  crystal in temperature interval 293-373K.

$T_{\text{exp}}, \text{K}$	Modification	Lattice parameters, Å			Z	Sp. gr.	V, Å <sup>3</sup>	$\rho$ , gr/cm <sup>3</sup>
		a	b	c				
290	$\text{Cu}_2\text{Te}$ - orthorhomb.	7.319	22.236	36.458	104	P2 <sub>1</sub> /n	5933.368	7.407
	$\text{CuAgSe}$ -orthorhomb.	4.107	20.421	6.299	10	P4/nmm	528.058	7.883
	Cubic	7.715			8	Fd3m	459.206	7.94
373	$\text{Cu}_2\text{Te}$ - orthorhomb.	7.329	22.361	36.515	104	P2 <sub>1</sub> /n	5975.440	7.355
	$\text{CuAgSe}$ -orthorhomb.	4.110	20.442	6.322	10	P4/nmm	531.153	7.82
	Cubic	7.729			8	Fd3m	461.711	7.90
473	Cubic	7.759			8	Fd3m	467.108	7.81

The many reflexes from observable three phases on diffractogram collide to each other. The distribution of anions (Se and Te) and cations (Cu and Ag) correspondingly is the reason of the fact that crystal  $\text{CuAgSe}_{0.5}\text{Te}_{0.5}$  is multiphase one. The stove had been switched on and through each 50K the records had been carried out after diffractogram record at room temperature. At these conditions the sample stays three-phase one and at  $444 \pm 1\text{K}$  the both orthorhombic modifications  $\text{Cu}_2\text{Te}$  and  $\text{CuAgSe}$  transform into cubic modifications. The transformation is reversible on, i.e. the sample transforms into initial state at cooling.

The temperature dependences of lattice parameters of elementary cells of all phases for  $\text{CuAgSe}_{0.5}\text{Te}_{0.5}$  existing in temperature interval 293-673K are graphically presented on fig.6 and in table 11. From fig.6 it is seen that parameters of both orthorhombic and cubic phases in the dependence on temperature increase linearly. The parameter  $a_k = f(T)$  doesn't deviate from linearity at transformation of both orthorhombic phases into cubic one. From this it is followed that cubic phase plays the role of completed ingot at transformation of both orthorhombic phases into cubic one.

From temperature dependence of lattice parameters the thermal expansion coefficients of both orthorhombic and cubic modifications which are presented in table 12.

The thermal expansion coefficient in orthorhombic phase crystallized in  $\text{Cu}_2\text{Te}$  structure in [100] direction is negative one. From this it is followed that strong anisotropy of thermal expansion is the one of the main reasons of lattice instability of both orthorhombic phases.

At exchange of anions in  $\text{CuAgSe}$  crystal, i.e. at exchange of  $1/2$  of Se atoms by tellurium atoms the obtained crystals of  $\text{CuAgSe}_{0.5}\text{Te}_{0.5}$  at room temperature consist in three phases. The transformations in  $\text{CuAgSe}_{0.5}\text{Te}_{0.5}$  are reversible ones and take place by type of single crystal – single crystal. Note that partial exchange of anions in  $\text{CuAgSe}$  crystal decreases the transformation temperature. In  $\text{CuAgSe}$  crystal the low-temperature orthorhombic modification at 504K transforms into HCC modification, in  $\text{CuAgSe}_{0.5}\text{Te}_{0.5}$  crystal the both orthorhombic phases at 444K transform into HCC modification.

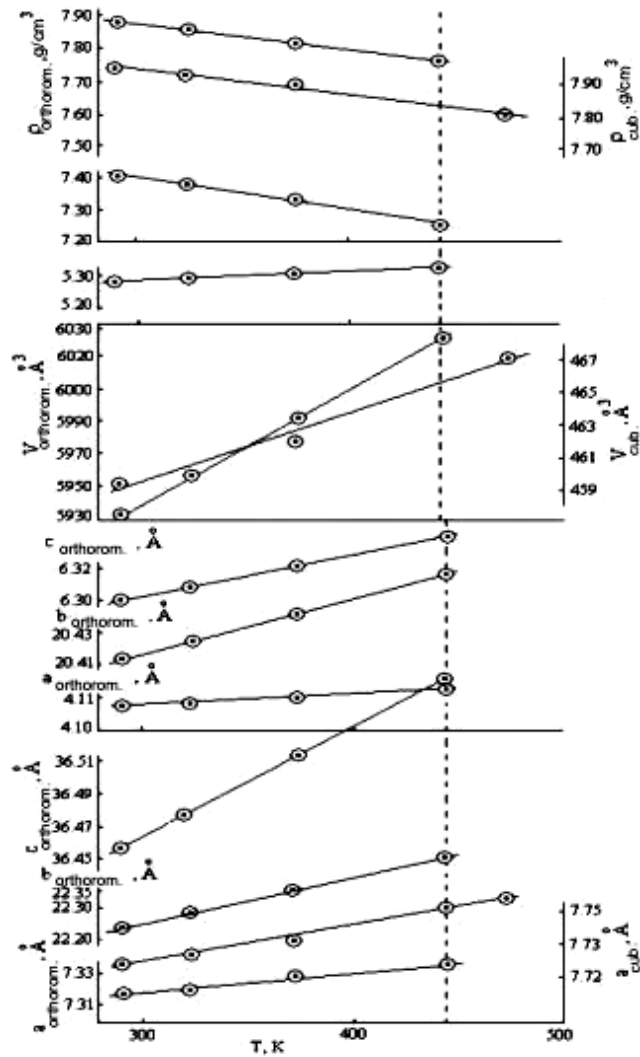


Fig.6. Temperature dependence of crystal lattice parameters, volume and strength of both orthorhombic and cubic modifications of CuAgSe<sub>0.5</sub>Te<sub>0.5</sub>.

Table 12.

Thermal expansion of CuAgSe<sub>0.5</sub>Te<sub>0.5</sub> crystal modifications.

T, K	$\alpha_{[100]} \cdot 10^6 K^{-1}$	$\alpha_{[010]} \cdot 10^6 K^{-1}$	$\alpha_{[001]} \cdot 10^6 K^{-1}$	$\bar{\alpha} = \frac{\alpha_{[100]} + \alpha_{[010]} + \alpha_{[001]}}{3} \cdot 10^6 K^{-1}$	$\beta = \alpha_{[100]} + \alpha_{[010]} + \alpha_{[001]} \cdot 10^6 K^{-1}$
290-373	16.462	67.729	18.837	34.343	103.028
290-473	8.801	17.708	43.992	23.500	70.501
290-373	21.863			21.863	65.589
290-473	31.165			31.165	93.495

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**$\text{Cu}_{2-x}\text{A}_x\text{Se}$  ( $x=0, 0.2, 0.4$ ;  $\text{A}=\text{Ag, Zn}$ ),  $\text{CuAgSe}$ ,  $\text{CuAgSe}_{0.5}(\text{S,Te})_{0.5}$  KRİSTALLARINDA TERMİK  
GENİŞLƏNMƏ VƏ POLİMORF KEÇİDLƏR**

$\text{Cu}_{2-x}\text{A}_x\text{Se}$  ( $x=0, 0.2, 0.4$ ;  $\text{A}=\text{Ag, Zn}$ ),  $\text{CuAgSe}$ ,  $\text{CuAgSe}_{0.5}(\text{S,Te})_{0.5}$  birləşmələri sintez edilmiş və Bricmen üsulu ilə monokristalları alınmışdır. 290-1000K temperatur intervalında yüksək temperaturlu rentgendifraktometrik metodla tədqiq olunan kristallardakı mövcud polimorf çevrilmələr aşkar edilmişdir. Qəfəs parametrlərinin temperatur asılılığından əsas kristalloqrafik istiqamətlərdə istidən genişlənmə əmsalları hesablanmışdır.

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**ТЕРМИЧЕСКИЕ РАСШИРЕНИЯ И ПОЛИМОРФНЫЕ ПЕРЕХОДЫ В КРИСТАЛЛАХ  
 $\text{Cu}_{2-x}\text{A}_x\text{Se}$  ( $x=0, 0.2, 0.4$ ;  $\text{A}=\text{Ag, Zn}$ ),  $\text{CuAgSe}$ ,  $\text{CuAgSe}_{0.5}(\text{S,Te})_{0.5}$**

Синтезированы и методом Бриджмена выращены монокристаллы  $\text{Cu}_{2-x}\text{A}_x\text{Se}$  ( $x=0, 0.2, 0.4$ ;  $\text{A}=\text{Ag, Zn}$ ),  $\text{CuAgSe}$ ,  $\text{CuAgSe}_{0.5}(\text{S,Te})_{0.5}$  и в интервале температур 290-1000К методом высокотемпературной рентгенодифрактометрии зафиксированы все существующие полиморфные превращения. Из температурной зависимости параметров решетки рассчитаны тепловые расширения по основным кристаллографическим направлениям.

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